

Furnace Injection of Alkaline Sorbents for Sulfuric Acid Control

Semi-Annual Technical Progress Report

April 1, 2002 – September 30, 2002

Cooperative Agreement No: DE-FC26-99FT40718

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Abstract

This document summarizes progress on Cooperative Agreement DE-FC26-99FT40718, Furnace Injection of Alkaline Sorbents for Sulfuric Acid Control, during the time period April 1, 2002 through September 30, 2002. The objective of this project is to demonstrate the use of alkaline reagents injected into the furnace of coal-fired boilers as a means of controlling sulfuric acid emissions. The coincident removal of hydrochloric acid and hydrofluoric acid is also being determined, as is the removal of arsenic, a known poison for NO_x selective catalytic reduction (SCR) catalysts. EPRI, the Tennessee Valley Authority (TVA), FirstEnergy Corporation, American Electric Power (AEP) and the Dravo Lime Company are project co-funders. URS Group is the prime contractor.

This is the sixth reporting period for the subject Cooperative Agreement. During previous reporting periods, two long-term sorbent injection tests were conducted, one on Unit 3 at FirstEnergy's Bruce Mansfield Plant (BMP) and one on Unit 1 at AEP's Gavin Plant. Those tests determined the effectiveness of injecting alkaline slurries into the upper furnace of the boiler as a means of controlling sulfuric acid emissions from these units. The alkaline slurries tested included commercially available magnesium hydroxide slurry (Gavin Plant), and a byproduct magnesium hydroxide slurry (both Gavin Plant and BMP). The tests showed that injecting either the commercial or the byproduct magnesium hydroxide slurry could achieve up to 70-75% overall sulfuric acid removal. At BMP, the overall removal was limited by the need to maintain acceptable electrostatic precipitator (ESP) particulate control performance. At Gavin Plant, the overall sulfuric acid removal was limited because the furnace injected sorbent was less effective at removing SO₃ formed across the SCR system installed on the unit for NO_x control than at removing SO₃ formed in the furnace. The SO₃ removal results were presented in the semi-annual Technical Progress Report for the time period April 1, 2001 through September 30, 2001. Additional balance of plant impact information for the two tests was reported in the Technical Progress Report for the time period October 1, 2001 through March 30, 2002. During the current reporting period, additional information became available about the effects of byproduct magnesium hydroxide injection on SCR catalyst coupons during the long-term test at BMP. These results are included in the current report. There was no other technical progress to report, because all planned testing as part of this project has been completed.

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1.0 INTRODUCTION

This document is the semi-annual Technical Progress Report for the project “Furnace Injection of Alkaline Sorbents for Sulfuric Acid Control,” for the time period April 1, 2002 through September 30, 2002. The objective of this project is to demonstrate the use of alkaline reagents injected into the furnace of coal-fired boilers as a means of controlling sulfuric acid emissions. The coincident removal of hydrochloric acid and hydrofluoric acid has also been determined, as has the removal of arsenic, a known poison for NO_x selective catalytic reduction (SCR) catalysts. The project is being funded by the U.S. DOE National Energy Technology Laboratory under Cooperative Agreement DE-FC26-99FT40718. EPRI, the Tennessee Valley Authority (TVA), FirstEnergy Corporation, American Electric Power Company (AEP), and the Dravo Lime Company are project co-funders. URS Group (formerly Radian International) is the prime contractor.

Sulfuric acid is present in most flue gases from coal combustion because a small percentage of the SO₂ produced from the sulfur in the coal (approximately 0.5% to 1.5%) is further oxidized to form SO₃. The SO₃ combines with flue gas moisture to form vapor-phase or condensed sulfuric acid at temperatures below 500°F. Because of this temperature effect, in this report sulfur in this oxidation state is generally referred to as “SO₃” in furnace gas or flue gas upstream of the boiler air heater, and “sulfuric acid” in flue gas downstream of the air heater.

Besides being a Toxic Release Inventory substance and a potential precursor to acid aerosol/condensable emissions from coal-fired boilers, sulfuric acid in the flue gas can lead to boiler air heater plugging and fouling, corrosion in the air heater and downstream, and the formation of a visible plume. These issues will likely be exacerbated with the retrofit of SCR for NO_x control on some coal-fired plants, as SCR catalysts are known to further oxidize a portion of the flue gas SO₂ to SO₃.

The project has tested the effectiveness of furnace injection of four different calcium- and/or magnesium-based alkaline sorbents on full-scale utility boilers for SO₃ control. These reagents have been tested during four one- to two-week tests conducted on two FirstEnergy Bruce Mansfield Plant (BMP) units. One of the sorbents tested was produced from a wet flue gas desulfurization (FGD) system waste stream, from a system that employs a modified Thiosorbic[®] Lime scrubbing process. The other three sorbents are commercially available.

After completing the four one- to two-week tests, the most promising sorbents were selected for two longer-term (up to 30-day) full-scale tests. The longer-term tests were used to confirm the effectiveness of the sorbent tested over extended operation, and to determine balance-of-plant impacts. Two longer-term tests were conducted, one on FirstEnergy’s BMP Unit 3 and the second on AEP’s Gavin Plant Unit 1.

At the completion of the project, it is expected that sufficient full-scale test data will be available to design and implement commercial installations of the sulfuric acid control technologies demonstrated.

The remainder of this report is divided into three sections. Section 2 provides a summary account of progress on the project during the current reporting period, including any problems encountered. Section 3 provides a forecast of plans for the next and future reporting periods, and Section 4 provides a detailed discussion of technical results from the project during the current reporting period.

2.0 PROGRESS DURING THE CURRENT REPORTING PERIOD

2.1 Summary of Progress

The current reporting period, April 1, 2002 through September 30, 2002, is the sixth technical progress reporting period for this project. October 1, 1999 was the start date for this Cooperative Agreement.

Last year, a long-term slurry injection test was conducted at BMP Unit 3. The sorbent was a byproduct magnesium hydroxide (byproduct Mg) produced at Allegheny Energy's Pleasants Power Station. The long-term injection test began the second week of May and continued into the first week of June 2001. The primary measure of the success of the slurry injection tests was the reduction in flue gas SO₃ concentration in the electrostatic precipitator outlet flue gas. After the test was complete, samples collected during the test were chemically analyzed, and data collected were organized, reduced and analyzed. Results from this testing were presented in a previous Technical Progress Report for this project (April 1, 2001 through September 30, 2001).

The test at BMP included an evaluation of the impacts of byproduct Mg injection in the furnace on SCR catalyst coupons inserted into the flue gas stream at the economizer outlet duct. Analyses and reporting on these coupons were completed during the current reporting period, and these results are summarized in Section 4 of this report.

Last July, AEP joined the project as a new team member, co-funder, and host site. Their Gavin Plant started up new SCR units for NO_x control on both Units 1 and 2 (both 1300-MW coal-fired units) in May 2001. As might have been expected, a portion of the SO₂ produced from the high-sulfur coal fired there was oxidized to SO₃ across the SCR catalysts. This conversion essentially doubled the amount of SO₃ in the flue gas going to the units' air heaters, and correspondingly increased sulfuric acid concentrations at the ESP outlet and FGD outlet (stack). The increased sulfuric acid concentrations in the stack flue gas caused increased plume opacity, and appeared to contribute to the occurrence of plume "touch downs" at ground level near the plant. AEP joined the project to test magnesium hydroxide injection as a means of controlling stack sulfuric acid concentrations, and TVA agreed to forego testing on one of their units for the opportunity to test sorbent injection on a unit with an operating, full-scale SCR system.

Because the supply of byproduct Mg in the quantities required to treat two 1300-MW units was in question, AEP also wanted to test commercial magnesium hydroxide (commercial Mg), so that sorbent was used for a portion of the test. The testing at Gavin Plant was conducted from the middle of August through the first week of September. SO₃ removal results from this test were reported in a previous Technical Progress Report for this project (April 1, 2001 through September 30, 2001). Balance-of-plant results from the testing at Gavin Plant were presented in a later Technical Progress Report (October 1, 2001 through March 31, 2002). There are no additional results from the Gavin testing to report for the current period.

No subcontracts were issued or completed during the current reporting period.

One draft topical report was submitted during the current reporting period, covering the results of the long-term sorbent injection tests conducted at BMP and at Gavin Plant in the late spring and summer of 2001. Also, a poster presentation on results from this project was made at a NETL-sponsored PM_{2.5} conference in April.

2.2 Problems Encountered

There were no problems encountered during the current reporting period.

3.0 PLANS FOR FUTURE REPORTING PERIODS

3.1 Plans for Next Reporting Period

The next reporting period will cover the time period October 1, 2002 through March 31, 2003. Since the new end date for the Cooperative Agreement is December 31, 2002, the next reporting period will actually just cover three months. During the next reporting period, the final report for the project will be prepared and submitted.

3.2 Prospects for Future Progress

Any subsequent reporting period would extend beyond the current period of performance of this Cooperative Agreement, which ends December 31, 2002. Therefore, no progress is anticipated beyond that planned for the next reporting period.

4.0 TECHNICAL RESULTS

The technical results for the current reporting period (April 1, 2002 through September 30, 2002) are limited to additional results that have become available for one of the two longer-term (25-day) alkaline slurry injection tests that were conducted during 2001. One test was conducted on BMP Unit 3 in May/June 2001, and the second was conducted on AEP's Gavin Plant Unit 1 in August/September 2001. The first test evaluated a byproduct magnesium hydroxide [$\text{Mg}(\text{OH})_2$] (byproduct Mg) as a furnace injection sorbent for SO_3 control. The second, at Gavin Plant, evaluated both the byproduct Mg and commercially available magnesium hydroxide (commercial Mg) as furnace injection sorbents for SO_3 control.

The remainder of this section presents and discusses additional results from the BMP tests that have become available during the current reporting period. There is no new information available from the Gavin long-term test.

4.1 Long-term Test on BMP Unit 3

During this previous long-term test, byproduct Mg slurry was injected into the entire Unit 3 boiler continuously for 23 days, to assess its effectiveness for flue gas SO_3 control.

Various analytical techniques were used to assess the effects of sorbent injection. These primarily included sampling with the Controlled Condensation System (CCS) method for determining flue gas SO_3 content and, to a lesser extent, an acid dew-point (ADP) meter for determining the sulfuric acid dew point (and, indirectly, the concentration of sulfuric acid) of the flue gas. Daily average SO_2 concentration measurements were often made coincident with the CCS measurements. EPA Reference Method 26a was used for determining hydrochloric acid (HCl) and hydrofluoric acid (HF), as well as chlorine (Cl_2) and fluorine (F_2) concentrations in the ESP outlet flue gas. A modified version of EPA Method 108 was used to determine flue gas vapor-phase and particulate arsenic concentrations at the economizer outlet. Impacts on ESP operation were quantified by taking voltage and current data on operating electrical sections of the Unit 3 ESPs. Sorbent and ESP hopper samples were analyzed for magnesium content and sulfate content, for density and weight percent solids, and for total alkalinity. Coal samples were collected and analyzed for a variety of parameters according to ASTM protocols. Visual observations were made of boiler furnace and pendant superheater tube surfaces prior to and during sorbent injection to observe any trends related to slag formation.

All of the above results have been previously reported. The reader is referred to a previous Technical Progress Report for this project (April 1, 2001 through September 30, 2001) for details of BMP Unit 3, test descriptions, SO_3 removal results, and balance-of-plant impacts. The only new information related to this testing that has become available for reporting during the current reporting period is the results of analyses of SCR catalyst coupons that were inserted into the BMP Unit 3 ductwork during the long-term test. These results are presented and discussed below.

4.1.1 Effect of Byproduct Mg on SCR Catalyst Coupons

At the beginning of the long-term tests at BMP, a number of SCR catalyst coupons provided by an SCR catalyst vendor, Babcock-Hitachi K.K., were inserted into the economizer outlet duct to be removed at prescribed time intervals as the test progressed. These coupons were recovered at the prescribed times and analyzed for a number of chemical and physical parameters as described below in an effort to predict the effects of byproduct Mg injection in the furnace on a downstream SCR system.

There were concerns that these coupon results would not be an accurate predictor of full-scale effects for a number of reasons including the relatively short duration of the byproduct Mg injection test (about 550 hours) versus SCR catalyst life. Also, the coupons were installed and exposed at duct velocities (50 to 60 ft/sec [15 to 18 m/s]) versus typical SCR operating velocity (about 13 to 17 ft/sec [4 to 5 m/s]), which could cause metals to penetrate further into catalyst pores. Finally, the small size of the coupons meant that edge effects could overstate effects that might be seen on full-length catalyst beds. In spite of these concerns, it was felt that collecting this information might at least indicate any major trends. Based on the results described below, it would have been desirable to have byproduct Mg injection coupons exposed for greater periods of time, but the concerns about duct velocity and coupon size do not appear to have influenced the results.

The coupons were inserted into a common area of the economizer outlet duct shortly after byproduct Mg injection began on May 11, 2001. Coupons were pulled on May 15 (101.5 hrs), May 20 (221.5 hrs), and May 31 (485.5 hrs) or after nominally 100, 200, and 500 hours of byproduct Mg testing. These coupons were shipped to Babcock-Hitachi and analyzed for the following parameters:

- Catalyst activity – the NO_x reduction activity of each catalyst coupon was measured with a micro-reactor under standardized test conditions;
- Physical properties – specific surface area was measured by the B.E.T. method, and pore volume was measured by the mercury adsorption method; and
- Chemical composition – the chemical composition of the catalyst surface was measured semi-quantitatively by x-ray fluorescence (14 metals plus chlorine and sulfate), and quantitative analyses were conducted on digested samples for 10 metals plus chlorine and sulfate.

The results of these analyses are presented below and compared to previous results for baseline (no sorbent injection) coupons from BMP Unit 3.

4.1.1.1 Catalyst Activity

Figure 4-1 compares the NO_x reduction results for the catalyst coupons from the byproduct Mg test to results for baseline (no injection) samples from the same exposure periods. In both sets of coupons the loss of activity with time is very gradual. There does not appear to be any difference in the rate of activity loss for the baseline versus the byproduct Mg test coupons.

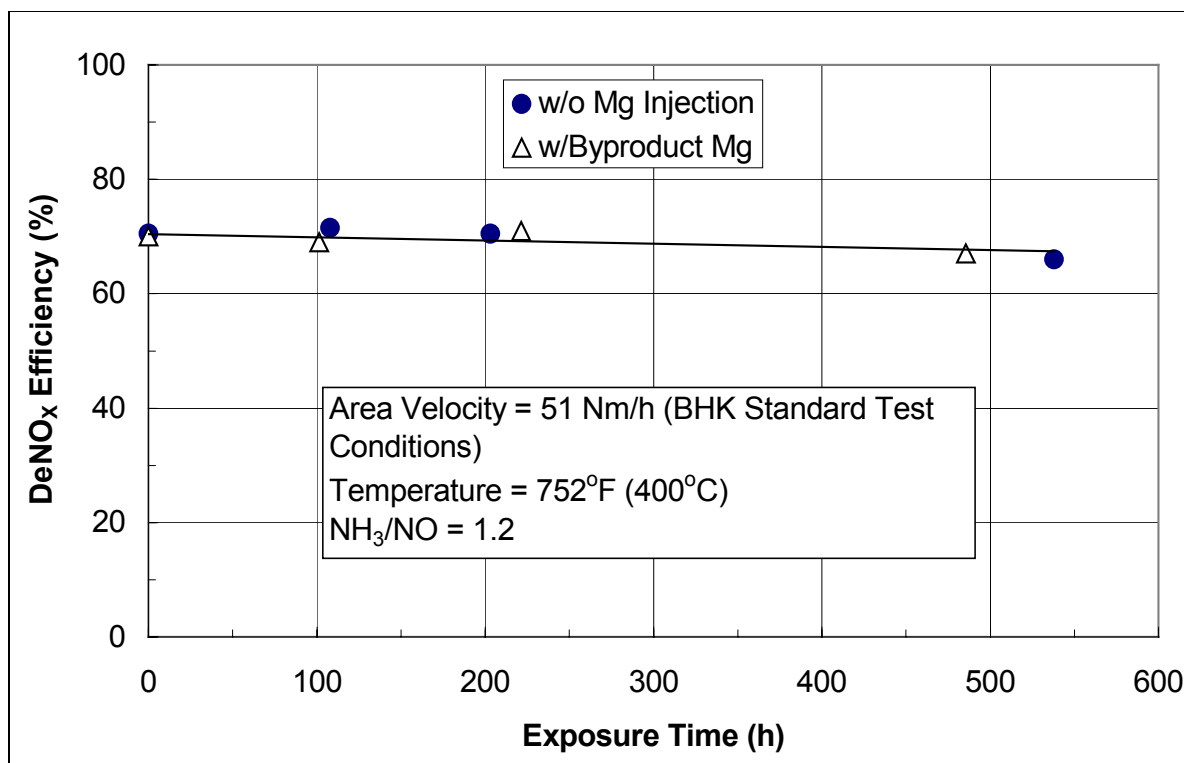


Figure 4-1. Catalyst Coupon NO_x Reduction Activity for Baseline and Byproduct Mg Tests Versus Flue Gas Exposure Time, BMP Unit 3

4.1.1.2 Physical Properties

Table 4-1 summarizes the results of the physical property measurements. The surface area and pore volume results are presented in relative terms compared to unexposed coupons since the actual values for these two parameters are considered proprietary. The results show some loss in specific surface area under both conditions but somewhat less surface area loss for the byproduct Mg injection test coupons than the baseline (no injection) coupons at 200 and 500 hours. The byproduct Mg injection coupons showed slightly greater specific surface area loss at 100 hours, which may be an anomaly. Reduced specific surface area loss at longer duration is considered a desirable outcome because loss of surface area can ultimately lead to activity loss. The relative pore volume results show very similar values for both the baseline and byproduct Mg injection test coupons, with very little loss of pore volume in either.

4.1.1.3 Chemical Composition Results

Results of the semi-quantitative and quantitative chemical analyses are summarized in Tables 4-2 and 4-3, respectively. Again, data are shown for varied flue gas exposure times for both baseline coupons and coupons from the byproduct Mg injection test.

Table 4-1. Summary of BMP Unit 3 Catalyst Coupon Physical Property Measurements

Time of Flue Gas Exposure	Relative Specific Surface Area		Relative Pore Volume	
	Baseline	Byproduct Mg Injection	Baseline	Byproduct Mg Injection
Unused Coupon	1.00	1.00	1.00	1.00
100 hours	0.92	0.89	1.00	1.01
200 hours	0.91	0.97	0.99	1.01
500 hours	0.91	0.97	0.98	0.99

Table 4-2. Summary of Semi-quantitative (Surface) Chemical Analyses on BMP Unit 3 Catalyst Coupons

Coupon Type	Unused	Baseline (without Injection)				With Byproduct Mg Injection		
Flue Gas Exposure Duration	0 h	100 h	200 h	500 h	101.5 h	221.5 h	485.5 h	
Chemical Composition (wt%)								
Na ₂ O	0.025	0.038	0.051	0.083	0.048	0.056	0.080	
MgO	-	0.066	0.069	0.12	0.28	0.18	0.24	
Al ₂ O ₃	2.7	3.5	3.8	4.9	5.1	4.8	5.2	
SiO ₂	7.4	9.1	9.5	11	14	14	16	
P ₂ O ₅	0.16	0.18	0.18	0.27	0.19	0.22	0.17	
SO ₃	-	1.3	1.4	1.9	3.3	2.2	3.0	
Cl	0.042	0.038	0.041	0.023	0.045	0.042	0.041	
K ₂ O	Trace	0.062	0.053	0.064	0.11	0.082	0.084	
CaO	0.033	0.17	0.14	0.22	0.35	0.27	0.45	
Cr ₂ O ₃	0.17	0.13	0.15	0.12	0.21	0.62	0.24	
Fe ₂ O ₃	0.094	0.64	0.81	0.66	1.2	2.3	1.2	
NiO	-	0.011	Trace	Trace	0.015	0.012	0.016	
As ₂ O ₃	-	0.13	0.24	0.62	Trace	0.026	0.037	
SrO	-	-	-	Trace	Trace	Trace	Trace	
ZrO ₂	0.065	0.068	0.056	0.62	0.048	0.025	0.050	
Nb ₂ O ₅	0.16	0.16	0.15	0.16	0.12	0.15	0.11	

Table 4-3. Results of Quantitative (Bulk) Chemical Analyses of BMP Unit 3 Catalyst Coupons

Coupon Type	Unused	Baseline (without Injection)			With Byproduct Mg Injection		
Flue Gas Exposure Duration	0 h	100 h	200 h	500 h	101.5 h	221.5 h	485.5 h
Chemical Composition (wt%, except where noted)							
Na ₂ O	0.03	0.032	0.036	0.042	0.031	0.031	0.035
MgO	0.033	0.033	0.033	0.033	0.022	0.022	0.020
Al ₂ O ₃	7.16	7.29	7.26	6.80	7.63	7.82	7.41
SiO ₂	12.66	13.60	13.33	12.17	13.58	13.43	12.96
P ₂ O ₅	0.052	0.060	0.056	0.074	0.023	0.046	0.046
SO ₃	0.17	0.76	0.80	0.84	1.27	1.07	0.91
Cl	0.009	0.006	0.008	0.007	0.009	0.007	0.005
K ₂ O	0.0024	0.014	0.020	0.031	0.014	0.016	0.017
CaO	0.024	0.042	0.049	0.073	0.055	0.046	0.038
Fe ₂ O ₃	0.043	0.19	0.29	0.27	0.200	0.172	0.114
As ₂ O ₃	0.026	0.066	0.13	0.24	<0.013	<0.013	0.013
V ₂ O ₅ *	Base	NR**	NR**	NR**	+4%	+6%	+8%

* Percent difference in concentration from unused catalyst.

**Not reported.

The results of the semi-quantitative surface analyses in Table 4-2 show the following trends:

- Accumulation of sodium (Na), potassium (K), calcium, magnesium, iron (Fe), phosphorus (P), sulfur, silicon (Si) and aluminum (Al) was apparent in both types of coupons;
 - Of these species, calcium, magnesium, iron, sulfur, and silicon accumulations were clearly greater on the byproduct Mg test coupons,
 - The increased calcium, magnesium, and sulfur accumulations are most likely due to the byproduct Mg injection (Mg(OH)₂ and CaSO₄•2H₂O), but still the increases were relatively small, and
 - The iron and silicon increases are most likely from fly ash;
- Accumulation of arsenic (As) was apparent in the baseline coupons, but not in the byproduct Mg test coupons;
 - This may indicate that the byproduct Mg reduced vapor phase arsenic concentrations, and
 - Reduced arsenic accumulation on the catalyst surface is seen as a positive impact, since arsenic is a known SCR catalyst poison.

The quantitative (bulk coupon) analysis results in Table 4-3 showed following tendencies:

- Both types of coupons showed accumulations of sodium, sulfur, potassium, calcium, and iron;
- Of those species, for the longest duration (500-h) samples only sulfur accumulations were higher in the byproduct Mg coupons;
- Neither set of coupons showed magnesium concentration increases.
- The byproduct Mg test coupons showed accumulation of aluminum and silicon (fly ash components), but the baseline samples did not;
- As shown in the XRF analysis results, there was little or no accumulation of arsenic compared to that in the baseline samples; and
- Small increases in vanadium (V) concentration were observed for the byproduct Mg test coupons. The actual concentration results are not shown, nor are the baseline sample results, because this information is considered proprietary.

4.2 Conclusions from SCR Coupon Evaluations

According to these analysis results, over a period of 500 hours the activity decrease tendency in the catalyst coupons from the byproduct Mg test at BMP Unit 3 was similar to baseline test results. Physical property changes in the two samples sets were also similar, although the surface area decrease tendency was slightly less in the byproduct Mg test coupons. These results suggest that over the period evaluated, the byproduct Mg injection had little or no impact on the SCR catalyst coupons.

However, two items were noted in the chemical analyses of the coupons that may forecast longer-term impacts of byproduct Mg injection. First, the accumulation of arsenic on the catalyst coupons was apparently less during the byproduct Mg tests than during baseline operation. This is a potential benefit from byproduct Mg injection, as arsenic is a known SCR catalyst poison. Thus, catalyst life could be extended with byproduct Mg injection compared to operation without sorbent injection.

However, an increase in vanadium content was observed over the duration of the byproduct Mg test, while no increase was seen in the baseline coupons. This suggests that SO_2 to SO_3 conversion across the SCR catalyst might increase with operating time, since vanadium is a known SO_2 oxidation catalyst. Such an increase, if realized, would be counterproductive to byproduct Mg injection in the furnace to lower flue gas SO_3 /sulfuric acid concentrations.